Rare Metal Materials and Engineering
Volume 45, Issue 9, September 2016
Online English edition of the Chinese language journal

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(9): 2269-2274.

ARTICLE

Research Progress in Magnesium Alloys as Functional Materials

Chen Xianhua[1,2], Geng Yuxiao[1], Pan Fusheng[2,3]

[1] Chongqing University, Chongqing 400045, China; [2] National Engineering Research Center for Magnesium Alloys, Chongqing 400045, China; [3] Chongqing Academy of Science and Technology, Chongqing 401123, China

Abstract: Magnesium alloys have a significant advantage, low density over other structure metals currently and have been widely used in various fields such as transportation and aerospace. With the development of research and the enlargement of research scope, more advantages have been developed: high storage capacity, high theoretical volumetric energy density, extraordinarily high damping capacity, good biocompatibility, excellent shielding efficiency as well as impressive thermal conductivity. Therefore Mg alloys have the potential to be various functional materials, such as hydrogen storage material, rechargeable electrochemical batteries, damping material, biodegradable implant material, electromagnetic shielding material, and thermal conductive material. Unfortunately, each kind of functional material has bottlenecks needing to be broken through, and a lot of researches have to be carried out. This review comprehensively covers the research progress and the up-to-date summary of Mg and Mg alloys as functional materials in recent years. The six kinds of functional materials above all will be discussed.

Key words: magnesium alloys; functional materials; novel processing; properties; alloying

Magnesium alloys are getting speedy development in recent years because of their inherent advantages such as low density and high specific strength[1]. With the development of researches, numerous appealing properties of Mg and its alloys are found and they are considered to be the promising candidates for functional materials in various applications because of the special advantages compared to other alloys [1-5]. For example, Mg alloys have high storage capacity, so their hydrides are promising to be hydrogen carriers. Pure Mg, Mg-Ni, Mg-Al, and Mg-Re etc. have been developed as Mg hydrogen storage materials. In addition, Mg is expected to be an alternative to lithium in the future ion-transfer batteries duo to its higher safety and lower cost. Mg-*M*-B (*M*=Co, Ni, Fe, ·····) and Mg-*M*-SiO_4 (*M*=Mn, Fe, Co) were investigated as positive electrode materials for magnesium batteries. Mg alloys' damping capacity is excellent, so they can be used in anti-vibration and noise-reduction applications. Mg alloys also exhibit good biocompatibility and are ideal implant materials because the content of magnesium in cells is the second largest, and the mechanical properties are close to those of natural bone. Mg-Ca and Mg-Sr series alloys coated by calcium phosphate or hydroxyapatite (HA) exhibit appropriate corrosion rate and good biocompatibility, and reach the requirement of an ideal implant material. What's more, Mg alloys are prominent candidate materials to reduce the harm of electromagnetic wave because of their high electromagnetic shielding performance. And the good thermal conductivity makes them have the potential to be radiator materials. However, there are still many problems to be solved for implementing functional Mg alloys widely. Considerable researches have focused on specific functional properties of Mg alloys and some alloy series have been investigated in particular areas. The present paper will focus on the research progress of magnesium alloys in these aspects, and the research hotspots and the development tendency of further research is summarized in detail. Such a review can provide

Received date: September 19, 2015
Foundation item: International Science & Technology Cooperation Program of China (2014DFG52810); National Natural Science Foundation of China (51571043); Fundamental Research Funds for the Central Universities (106112015CDJZR135515)
Corresponding author: Chen Xianhua, Ph. D., Professor, College of Materials Science and Engineering, Chongqing University, Chongqing 400045, P. R. China, Tel: 0086-23-65102633, E-mail: xhchen@cqu.edu.cn

important information for further development of Mg alloys as functional materials.

1 Hydrogen Storage Materials

Hydrogen gas will be the most promising fuel in the future because it is the most abundant resource and green in energy. Hydrogen can be stored as pressurized gas, cryogenic liquid, and solid state hydrogen. Solid-state storage is more economic and safer than gas and liquid storage methods, and many efforts have been made to research solid materials. The US Department of Energy (DOE) proposed a target: the optimal desorption temperature ranges from 60 to 120 °C as well as the hydrogen storage capacity is 6.5 wt% at least [6,7].

Mg is a promising candidate for hydrogen storage in various applications due to its light weight, high storage capacity, reversibility and recyclability. Mg alloys combine chemically with hydrogen to form hydrides that are known as Mg hydrogen-storage materials. In the past decade, a series of hydrides have been prepared, such as Mg_2NiH_4, Mg_2FeH_6, $Mg(AlH_4)_2$ and some unusual metal hydride Mg_2CoH_5, Mg_3ReH_7, Mg_3CrH_6. However, Mg alloy hydrides are still far from meeting the need for practical applications because of high hydrogen discharge temperature, complicated synthesis process, slow desorption kinetics and high reactivity toward air and oxygen [7-9].

Corresponding to the challenges in application, lots of researches have been carried out to find viable solutions to optimize hydrogenation properties. The commercial hydrogen storage and utilization can be achieved by decreasing the temperature of hydrogen desorption, enhancing the kinetics and improving the cycle life span. Alloying and microstructure modification are the main approaches to improve the hydriding properties [10-12]. Shao et al reported that Mg-Co alloys present high hydrogen storage capacity of around 3 wt%[10], which is obviously higher than that of $TiFe_{0.86}Mn_{0.1-x}Co_x$ alloys (1.98 wt%) [13]. It was found that the hydrogenation kinetics and the H-storage capacity are dependent on the microstructure and phase composition of the alloys. Large grain boundary area as well as small particle sizes are beneficial to decrease the desorption energy and to reduce the desorption temperature[14-16]. Ballmilling is a main synthesis technique and widely applied to produce hydrogen storage materials. A large amount of fresh surface and defects produced during milling process are contributed to the kinetics enhancement. The nanostru- ctured composites alloying with other transition metals and their oxides can also reduce the desorption temperature and improve the thermodynamic. However, nano-sized Mg is sensitive to oxygen, which is very dangerous and difficult to store and deliver [14-16]. A core-shell structured Mg based nano-composite is an ideal solution to protect the surface of nano-sized Mg for the sake of safety [10, 11]. J. X. Zou et al. developed a core-shell structured Mg based nano-composite with the surface of Mg particles covered by MgO, RE_2O_3 nano-grains, which significantly improved hydrogen storage thermodynamic, kinetic and anti-oxidation properties [6].

The absorption/desorption kinetics can also be improved by adding catalyst. It was known that some metals and transition metal oxides (such as Al, Fe, Ti, B, Zr, Nd_2O_5 and V_2O_5) could be efficient additives. For example, $Mg_{2-x}Al_xNi$ ($x\leqslant 0.1$) has lower desorption temperature and faster desorption rate than Mg-Ni. Adding Nb_2O_5 especially nanocrystalline Nb_2O_5 in MgH_2 improves desorption capacity and cyclic stability significantly [16-18].

2 Rechargeable Magnesium Batteries

Lithium ion batteries play an important role in the field of portable electronic devices, electric vehicles (EV) and other energy storage systems. However, the safety and high cost are the main disadvantages that have not been resolved, since the electrolyte is easy to burn and Li is expensive [19, 20]. Consequently finding new types of batteries with greater safety and lower cost is urgent. The theoretical volumetric energy density of Mg-ion batteries is 3832 $mAh\cdot cm^{-3}$ higher than that of Li (2061 $mAh\cdot cm^{-3}$), and Mg is relatively cheaper and safer than Li. Mg is expected to be an alternative to lithium in the future ion-transfer batteries. Since Aurbach et al. made a complete Mg rechargeable battery in 2000, more and more research institutions turned their sight to magnesium batteries [19-23].

Suitable electrodes for magnesium ion insertion, de-insertion and conducting electrolytes are critically important for Mg rechargeable batteries. While the Mg-ion is difficult to diffuse in solid-state electrode compared to the Li-ion, and the corrosion resistance of the magnesium battery is low. The reactions of the anode with electrolyte would produce a blocking layer, which limits the achievable battery voltage and leads to the poor cycling ability of Mg batteries. For Mg batteries, the choice of electrolyte is also very critical. There are two aims in present research activities: one is to find suitable cathodes for magnesium ion insertion and de-insertion or commercially viable active materials for Mg-ion batteries; the other is to prepare suitable magnesium ion conducting electrolytes with sufficiently ionic conductivity [23-25].

Although a lot of researches have been carried out, the development of magnesium batteries is still at a preliminary stage, and their poor catalytic activity and low corrosion resistance still restrict their practical applications. The initial research activities focused on various potentially promising metal oxides (vanadium and molybdenum oxides), sulfides and other insertion compounds in organic solvents and low-temperature salt melts; then manganese dioxide (MnO_2) and its polymorphs, Mg-*M*-B (*M*=Co, Ni, Fe, ⋯⋯), Mg-*M*-SiO_4 (*M*=Mn, Fe, Co) were investigated as a positive electrode material for magnesium batteries [23]. Nevertheless, there is no Mg battery system that is comparable to the Li-ion battery in the overall performance at present [26,27]. It was